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On the two-phonon scattering of X-rays in aluminum

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With 2 figures in the text

SUMMARY

The contribution from the two-phonon processes to the intensity of diffuse X-ray scattering in crystals has been accurately calculated in the case of aluminum for three different directions of the scattering vector $\varkappa = \mathbf{k} - \mathbf{k}_0$, where $\mathbf{k}_0$ is the wave vector of the incident photon and $\mathbf{k}$ that of the scattered photon. The calculation is based directly on the dynamical equations for the lattice vibrations in the harmonic approximation. The only further approximation introduced is the assumption that the temperature is so high that the mean energy of every lattice vibration may be put equal to kT. Comparisons are made between this accurate calculation and different approximate calculations. This investigation is of interest for the determination of the frequency spectra of the lattice vibrations of crystals from the measured intensities of diffuse X-ray scattering.

Measurements of the intensities of diffuse X-ray scattering by a single crystal make it possible to determine the frequency spectrum of the crystal. For the general theory of this scattering we refer to Waller [1]. If one considers the forces between the vibrating atoms only in the harmonic approximation, the intensity of the thermal diffuse scattering can be expressed as a sum of terms with the following interpretation. The first term represents the contribution from scattering processes involving only one elastic wave (one-phonon processes), the second term involves two such waves (two-phonon processes), and so on. In general only the first two or three terms contribute appreciably to the intensity. The contribution from the one-phonon processes is simply related to the frequency spectrum of the crystal. Experimentally this intensity contribution is obtained from the value of the total measured intensity by subtracting the Compton-scattering and the two- and three-phonon scattering, effects from higher-phonon processes being negligible [2]. The terms which are to be subtracted are sometimes comparable to or even larger than the contribution from the one-phonon scattering processes [2].

The two-phonon scattering has until now been calculated approximately in various ways. Olmer [3, 4], in the case of aluminum, used the simple Debye model, i.e., assumed the crystal to be an ideal isotropic continuum, all the elastic waves to have equal mean velocities, and the dispersion curve[1] to be linear. Walker [2], also dealing with aluminum, assumed the crystal to be elastically isotropic but distinguished between longitudinal and transverse waves and introduced a sine-shaped dispersion curve. A priori it is difficult to know the accuracy of these kinds of approximations. This is for instance evident from the fact that Walker says that his approximation gives a value of the two-phonon scattering that is sometimes as much as three times that calculated by Olmer. The fact that an accurate calculation of the two-phonon scattering is essential for the reliability of the frequency spectrum obtained from X-ray intensity measurements has initiated the following detailed investigation of the two-phonon scattering intensity in aluminum. It is based directly on the dynamical equations of the lattice vibrations.

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[1] The dispersion curve is obtained by plotting the frequency as a function of the wave number.

For a monatomic cubic lattice at so high a temperature that every lattice vibration has approximately the mean energy kT, the differential scattering cross section per atom due to the two-phonon scattering is[1]

$$\frac{d\sigma}{d\Omega}=\frac{f_0^2 e^{-2M}\, V\, |\boldsymbol{\varkappa}|^4\, (kT)^2}{16\pi^3 m^2}\, I(\boldsymbol{\varkappa}) \left(\frac{d\sigma}{d\Omega}\right)_{\text{Thomson}} \tag{1}$$

where $\left(\frac{d\sigma}{d\Omega}\right)_{\text{Thomson}}$ is Thomson's expression for the differential scattering cross section of a free electron, and $I(\boldsymbol{\varkappa})$ is the integral.

$$I(\boldsymbol{\varkappa})=\sum_{\boldsymbol{\tau}} \int_{V_{\boldsymbol{\tau}}} \sum_{i,j=1}^{3} \frac{[\mathbf{C}_i(\mathbf{q})\cdot \mathbf{e}_{\varkappa}]^2\, [\mathbf{C}_j(\mathbf{q}')\cdot \mathbf{e}_{\varkappa}]^2}{\omega_i^2(\mathbf{q})\, \omega_j^2(\mathbf{q}')}\, d\mathbf{q} \tag{2}$$

Here the vectors $\mathbf{q}$ and $\mathbf{q}'$ are the wave vectors of the two phonons participating in the scattering process. The vector $\boldsymbol{\varkappa}$ is equal to the difference between the wave vector $\mathbf{k}$ of the scattered photon and the wave vector $\mathbf{k}_0$ of the incident photon. The vectors $\mathbf{q}$ and $\mathbf{q}'$ are to be chosen to lie within the first Brillouin zone and to fulfill the condition

$$\mathbf{q}+\mathbf{q}'=\boldsymbol{\varkappa}-\boldsymbol{\tau} \tag{3}$$

where $\boldsymbol{\tau}$ is a reciprocal lattice vector.[2] For each $\boldsymbol{\tau}$ the integration in (2) is therefore to be performed over the volume V_τ common to the first Brillouin zones centered on the scattering point (i.e., the endpoint of $\boldsymbol{\varkappa}$) and on the reciprocal lattice point (i.e., the endpoint of $\boldsymbol{\tau}$). When the sum over all possible $\boldsymbol{\tau}$ is performed, these volumes exactly fill the first Brillouin zone centered on the scattering point. The other notations appearing in (1) and (2) are defined as follows:

f_0 is the atomic scattering factor
e^{-2M} is the Debye-Waller temperature factor
m is the atomic mass
V is the volume of the direct unit cell
k is Boltzmann's constant
T is the absolute temperature
$\mathbf{e}_{\varkappa}$ is the unit vector in the direction of $\boldsymbol{\varkappa}$
$\omega_j(\mathbf{q})$, where $j=1, 2, 3$, are the frequencies of the three elastic waves corresponding to the phonon wave vector $\mathbf{q}$
$C_j(\mathbf{q})$, where $j=1, 2, 3$, are the amplitude vectors of the three elastic waves corresponding to the phonon wave vector $\mathbf{q}$. These amplitude vectors are normalized

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[1] For the general formulae we refer to Waller [1]. We remark that Walker's [2] formula (4) is the same as our formula (1).

[2] Our definition of the reciprocal lattice differs from the usual one. Cf. the text to Fig. 1.

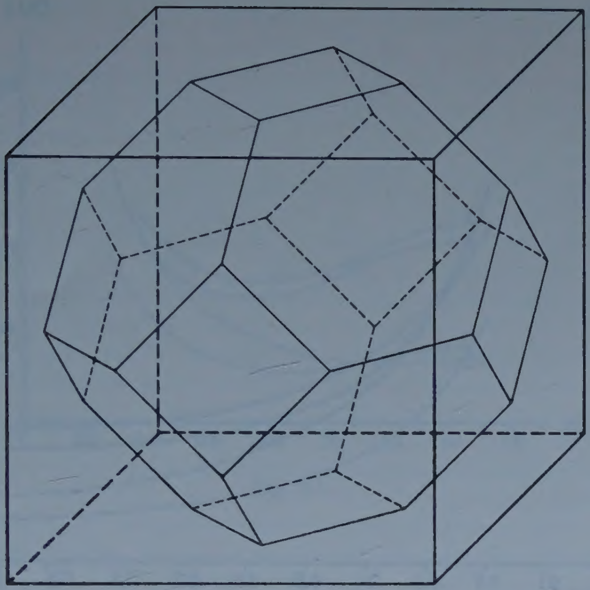

Fig. 1. This figure illustrates the relations in the reciprocal space of the aluminum lattice. The reciprocal lattice, which is body-centered cubic, has lattice points at the corners and at the center of the cube, the edge-length of which is $4\pi/a$. (According to the usual definition of the reciprocal lattice the edge-length is $2/a$, but we have introduced a factor 2π for convenience.) The polyeder represents the first Brillouin zone.

such that

$$\sum_j C_{jx} C_{jy} = \delta_{xy} \tag{4}$$

where δ_{xy} is the Kronecker symbol.

Starting from the dynamical equations for the vibrations of a monatomic lattice

$$\sum_y (D_{xy} - \delta_{xy}\omega_j^2) C_{jy} = 0 \tag{5}$$

where D_{xy} are quantities which depend on the interatomic forces, we transform (2) into a form which is more convenient for our purpose [1]. Multiplying (5) by $\frac{C_{jx}}{\omega_j^2}$, summing over j, and using (4), we get

$$\begin{aligned}
D_{xx}\sum_j \frac{C_{jx} C_{jx}}{\omega_j^2} + D_{xy}\sum_j \frac{C_{jx} C_{jy}}{\omega_j^2} + D_{xz}\sum_j \frac{C_{jx} C_{jz}}{\omega_j^2} &= 1 \\
D_{yx}\sum_j \frac{C_{jx} C_{jx}}{\omega_j^2} + D_{yy}\sum_j \frac{C_{jx} C_{jy}}{\omega_j^2} + D_{yz}\sum_j \frac{C_{jx} C_{jz}}{\omega_j^2} &= 0 \\
D_{zx}\sum_j \frac{C_{jx} C_{jx}}{\omega_j^2} + D_{zy}\sum_j \frac{C_{jx} C_{jy}}{\omega_j^2} + D_{zz}\sum_j \frac{C_{jx} C_{jz}}{\omega_j^2} &= 0
\end{aligned} \tag{6}$$

Solving this system of linear equations with respect to the quantities $\sum_j \frac{C_{jx} C_{jy}}{\omega_j^2}$,

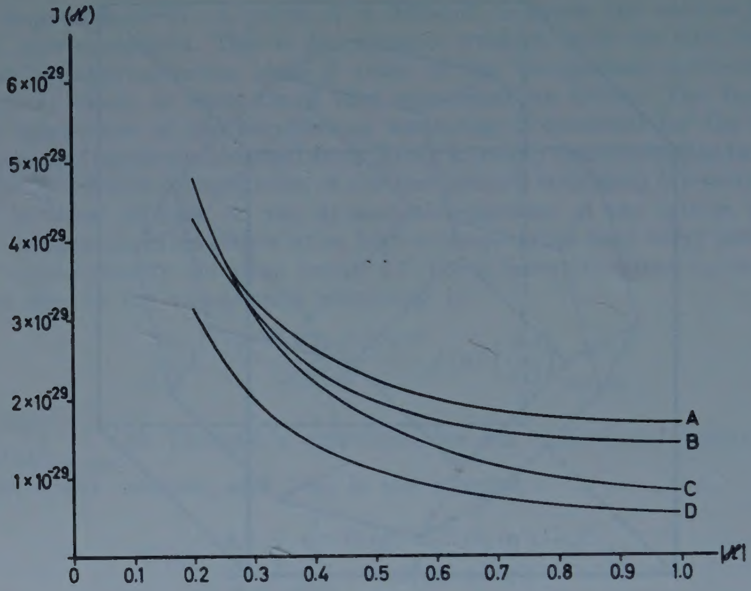

Fig. 2 a.

one gets

$$\sum_j \frac{C_{jx}(\mathfrak{q})\, C_{jy}(\mathfrak{q})}{\omega_j^2(\mathfrak{q})} = \frac{\Delta_{xy}(\mathfrak{q})}{\Delta(\mathfrak{q})} \tag{7}$$

where $\Delta(\mathfrak{q})$ denotes the determinant having the elements $D_{xy}(\mathfrak{q})$, and $\Delta_{xy}(\mathfrak{q})$ denotes the cofactor belonging to the element $D_{xy}(\mathfrak{q})$. Substituting (7) into (2), we obtain

$$I(\varkappa) = \int\limits_{\substack{\text{First Brillouin}\\ \text{zone}}} \frac{\left\{\sum\limits_{xy} e_{\varkappa x}\, e_{\varkappa y}\, \Delta_{xy}(\mathfrak{q})\right\} \left\{\sum\limits_{xy} e_{\varkappa x}\, e_{\varkappa y}\, \Delta_{xy}(\varkappa - \mathfrak{q})\right\}}{\Delta(\mathfrak{q})\, \Delta(\varkappa - \mathfrak{q})}\, d\,\mathfrak{q} \tag{8}$$

where use has been made of the facts that $\Delta(\mathfrak{q})$ and $\Delta_{xy}(\mathfrak{q})$ are periodic in the reciprocal lattice. This fact is immediately clear, for the elements $D_{xy}(\mathfrak{q})$ are known to have this periodicity.

We shall now consider the formula (8) for the case of aluminum, which has a face-centered cubic lattice. The reciprocal lattice is body-centered cubic, and the volume of integration in (8), which is the first Brillouin zone shown in Fig. 1, is limited by the planes

$$\left.\begin{matrix} q_x \\ q_y \\ q_z \end{matrix}\right\} = \pm \frac{2\pi}{a}, \qquad \pm|q_x| \pm |q_y| \pm |q_z| = \frac{3\pi}{a}$$

where q_x, q_y, and q_z are the cartesian components of the wave vector $\mathfrak{q}$, and a is the lattice constant. Considering only the forces between nearest and next nearest neighbours and assuming the forces of the latter kind to be central forces, one has

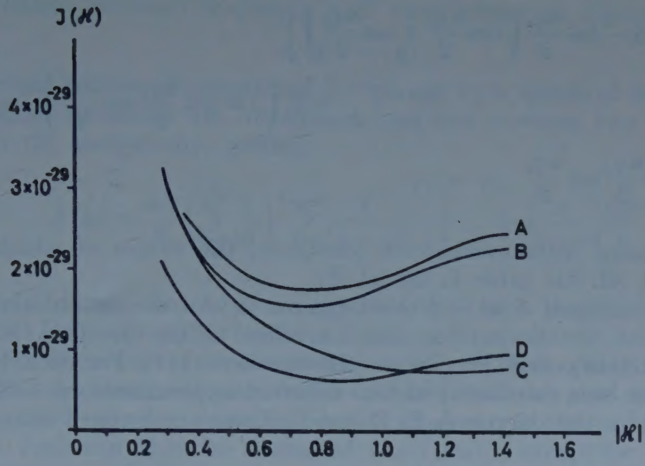

Fig. 2 b.

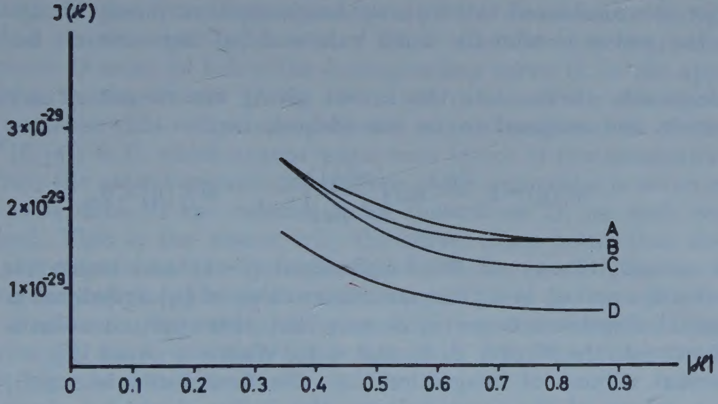

Fig. 2 c.

Fig. 2. This figure shows plots of $I(\varkappa)$, expressed in sec^4 cm^{-3}, as functions of $|\varkappa|$, expressed in units of $2\pi/a$, where a is the lattice constant. The figures 2a, 2b, and 2c refer to the cases that the scattering vector $\varkappa$ lies along the directions (100), (110), (111), respectively. Along these three directions $I(\varkappa)$ is symmetric with respect to the middlepoint of the line joining two neighbouring lattice points and is also periodic in the reciprocal lattice. The curves A, B, C, and D, which are drawn up to the symmetry point, have been obtained as follows:

A. Numerical evaluation of the integral (8).
B. Use of Walker's method for evaluating the integral (2).
C. Use of the simple Debye model for evaluating the integral (2).
D. Use of a simplification of Walker's method for evaluating the integral (2).

$$D_{xx}(\mathbf{q}) = \frac{4}{m}\left\{\alpha_1\left[2-\cos\frac{a\,q_x}{2}\left(\cos\frac{a\,q_y}{2}+\cos\frac{a\,q_z}{2}\right)\right]+\right.$$
$$\left.+\beta_1\left(1-\cos\frac{a\,q_y}{2}\cos\frac{a\,q_z}{2}\right)+\alpha_2\sin^2\frac{a\,q_x}{2}\right\}$$

$$D_{xy}(\mathbf{q}) = \frac{4}{m}\gamma_1\sin\frac{a\,q_x}{2}\sin\frac{a\,q_y}{2}$$

α_1, α_2, β_1, γ_1 being interatomic force constants, the values of which are taken from Walker [2] (cf. his table I, model B).

In Fig. 2 the integral $I(\boldsymbol{\varkappa})$ is plotted against $|\boldsymbol{\varkappa}|$ for the case of aluminum and for three different directions of $\boldsymbol{\varkappa}$. Fig. 2 a refers to the direction (100), Fig. 2 b to the direction (110), and Fig. 2 c to the direction (111). For each direction the integral $I(\boldsymbol{\varkappa})$ has been calculated in four different approximations, and the results are represented by the curves A, B, C, and D. These curves have been obtained as follows:

The curves A. These curves are obtained by computing the integral (8) numerically using an electronic computer.

The curves B. These curves are obtained according to a method which has been introduced by Walker [2] and in which the following approximations are made:

1°. The crystal is assumed to be an isotropic continuum, and consequently the phonon waves are considered to be purely longitudinal or purely transverse. This property of the waves is true for small values of $|\mathbf{q}|$ but certainly not for large values.

2°. The dispersion curves, i.e., the curves giving the frequency as function of the wave vector, are assumed to be sine-shaped, i.e.,

$$\omega_j(\mathbf{q}) = v_j\,\frac{2\,q_m}{\pi}\sin\left(\frac{\pi}{2}\frac{|\mathbf{q}|}{q_m}\right), \qquad 0 \leqslant |\mathbf{q}| \leqslant q_m \tag{9}$$

v_j being the sound velocity of the longitudinal ($j=1$) and transverse ($j=2, 3$) waves, respectively, and q_m being the maximum value of $|\mathbf{q}|$ as defined in 3° below. From the actual dispersion curve it is seen that this approximation is not good in all directions (cf. the figures 2, 3, and 4 in Walker's paper [2]).

3°. The actual volume of integration, i.e., the first Brillouin zone (Fig. 1) is replaced by a sphere of the same volume, the radius of which is denoted by q_m.

Walker's resulting formulae are given in the appendix in his paper [2] (cf. his eqs. (10) and his table II). Our curves B are calculated from the right-hand side of Walker's eq. (10), which we have, however, multiplied by the factor $\frac{\pi^3}{9\,q_m}\left(\sum_{j=1}^{3}\frac{1}{v_j^2}\right)^2$ in order to get values corresponding to our $I(\boldsymbol{\varkappa})$. Comparing the curves A and B, we see that Walker's approximate method gives astonishingly good results.

The curves C. These curves are obtained by using the simple Debye model for evaluating the integral $I(\boldsymbol{\varkappa})$. This means that the following approximations are made:

1°. The crystal is assumed to be elastically isotropic, but no distinction is made between longitudinal and transverse waves, i.e., $[\mathbf{e}_\varkappa \cdot \mathbf{C}_j(\mathbf{q})]^2$ is put equal to $1/3$ for all $j = 1, 2, 3$.

2°. The relation between frequency and wave vector is approximated by

$$\omega_j(\mathbf{q}) = v_j |\mathbf{q}| \tag{10}$$

3°. The actual volume of integration is replaced by a sphere of the same volume.

If these approximations are introduced, one can perform two of the three integrations in (2) analytically, getting

$$I(\boldsymbol{\varkappa}) = \frac{4\pi}{9}\left(\sum_{j=1}^{3}\frac{1}{v_j^2}\right)^2 \sum_{\boldsymbol{\tau}} \frac{1}{|\boldsymbol{\varkappa}-\boldsymbol{\tau}|} \int\limits_{1/2}^{q_m/|\boldsymbol{\varkappa}-\boldsymbol{\tau}|} \ln\left|\frac{x}{1-x}\right| \frac{dx}{x} \tag{11}$$

From this formula the curves C are obtained. It is seen that they give much too low values of $I(\boldsymbol{\varkappa})$, especially for large values of $|\boldsymbol{\varkappa}|$.

The curves D. These curves are obtained by modifying Walker's method (from which the curves B were obtained) such that we replace Walker's sine-shaped dispersion curves (9) by the linear dispersion curves (10) appearing in the simple Debye model. The integral $I(\boldsymbol{\varkappa})$ can then be evaluated analytically, except for one term which contains the integral (11) appearing in the simple Debye model. The curves D give still lower values of $I(\boldsymbol{\varkappa})$ than the curves C. The simple Debye model (curves C) is thus seen to give better values of $I(\boldsymbol{\varkappa})$ than the (in a sense more detailed) model used to obtain the curves D. The use of the linear approximation (10) for the dispersion curves causes $\omega_j(\mathbf{q})$ to be larger than its actual value, especially for large values of $|\mathbf{q}|$. In the linear approximation (10) the denominator $[\omega_i(\mathbf{q})\,\omega_j(\mathbf{q}')]^2$ of the integrand on the right-hand side of (2) is therefore too large, and it is clear that the curve D must lie below the corresponding curve B. In the approximation corresponding to the curves C the too large values of the denominator of the integrand are somewhat compensated by too large average values of the numerator $[\mathbf{C}_i(\mathbf{q})\cdot\mathbf{e}_\varkappa]^2\,[\mathbf{C}_j(\mathbf{q}')\cdot\mathbf{e}_\varkappa]^2$, which appear when each factor of this numerator is replaced by 1/3. When the actual angular dependence of the numerator is taken into account in detail, as is done in the calculation of the curves D, no such compensation is introduced. This is the reason why the curves C are better than the curves D. Although the approximation corresponding to the curves D gives too low values, these curves have approximately the right shape. It is in fact possible to get curves which are similar to the curves A by multiplying the values of $I(\boldsymbol{\varkappa})$, according to the curves D, by a constant factor of about 2.3. This corresponds to using, instead of (10), the formula

$$\omega_j(\mathbf{q}) \approx 0.8\, v_j |\mathbf{q}| \tag{12}$$

Finally I wish to thank Professor Ivar Waller for his support of this work. I am also much indebted to Dr. Alf Sjölander for many valuable discussions.

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